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COMPLETE SPECIFICATION

Block Copolymers of Formaldehyde and Process for preparing same

5 We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organized and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to polymers and to their preparation, and, more particularly, it relates to block copolymers containing polyoxymethylene groups.

15 In our United Kingdom Patent Specification No. 753,299, there are disclosed high molecular weight polyoxymethylenes possessing a high degree of thermal stability and toughness retention. In order to vary these and other properties for specific commercial uses it is desirable that copolymeric products be made available.

25 It is an object of this invention to provide block copolymers in which units of a polymeric substance are chemically bonded to units of polyoxymethylene. It is a further object of this invention to provide a process for preparing such block copolymers.

30 According to the present invention there is provided a block copolymer comprising 99%—10% by weight of one or more polyoxymethylene units, said units having a molecular weight of at least 4000, chemically joined to 1%—90% by weight of one or more polymeric units, which units are chemically different from polyoxymethylene, have a molecular weight of at least 500, are soluble in organic solvents and contain active hydrogen atoms as determined by the Zerewitinoff method.

40 The block copolymers of this invention are made by polymerizing substantially pure formaldehyde preferably of at least 99.9% purity, in the presence of one or more poly-

merization initiators and an organic solvent solution of a polymeric unit which is chemically different from polyoxymethylene, has a molecular weight of at least 500 and contains active hydrogen atoms as determined by the Zerewitinoff method. The formaldehyde polymerization initiator(s) is preferably employed in an amount of from 0.00001% to 0.3% by weight of the reaction medium.

45 A convenient way of operating is to sweep monomeric formaldehyde, at atmospheric pressure, through purifying traps held at -15° C., then into the top of a reaction chamber held at ordinary room temperature and containing a rapidly agitated cyclohexane solution of a formaldehyde polymerization initiator and active hydrogen-containing preformed polymer. The formaldehyde copolymer separates from solution as it is formed, and is isolated by filtration and vacuum drying at room temperature.

60 The polymerization can be operated on a continuous basis by continuously introducing formaldehyde, preformed polymer and fresh medium and initiator into the polymerization zone, while withdrawing polymerization slurry from the zone under steady state conditions.

70 The products of this invention are referred to as "block copolymers" since the polymer chain is believed to be made up of segments, or blocks, having the same recurring unit, namely, that present in the preformed polymer which is copolymerized with formaldehyde united by segments of a different structure derived from the formaldehyde. The correct structure of the copolymers is not known but it is believed that units within the copolymer are probably represented by the formula —R—(CH₂O)_nH, in which R has a molecular weight of at least 500 and represents the preformed polymer unit (minus the active hydrogens which may be removed in the process),

and x is a plural integer of at least 100. The polyoxymethylene unit, therefore, has a molecular weight of at least 4000.

The preferred copolymers are those derived from formaldehyde and preformed polymers containing two reactive hydrogens. This combination of reactants leads to the formation of linear, soluble, copolymers. Typical examples of preformed polymers containing two reactive hydrogens are the polyglycols.

The copolymers of this invention are characterized by good toughness, thermal stability, and plasticity which makes them useful in the plastic arts. Those derived by copolymerizing formaldehyde in the presence of polyglycols have a combination of clarity, flexibility and heat stability that makes them of special interest in the preparation of films and sheets.

In the case of copolymers containing residual hydroxyl groups, it is desirable to acylate them since this improves their thermal stability.

The examples which follow are submitted to illustrate and not to limit this invention. Parts are by weight unless otherwise stated.

EXAMPLE I

A. Purification of Formaldehyde

Highly purified gaseous monomeric formaldehyde was prepared from the hemiformal of cyclohexanol. The hemiformal was pumped at about 15 parts per minute into an insulated vessel which was heated sufficiently to maintain it one-half full of liquid. The vapors produced by decomposition of the hemiformal, comprising formaldehyde, cyclohexanol, and various impurities such as water, were led upward for about 2.5 feet through an insulated tube, then downward through a water-cooled bulb condenser, and then through a straight bore condenser, cooled by acetone circulating at -15°C . through the jacket. The condensate which collected at the bottom of the condenser was led to a recovery still.

The vapors were then passed upward through a bulb condenser, the interior walls of the condenser being covered with a downward flowing, countercurrent stream of heptane which had been freshly dried by passage through a silica gel column. The scrubbed gas was then passed through a vessel, cooled with an ice-water bath, to remove most of the heptane which had been picked up in the scrubber. Finally, the gas was passed through a series of three U-tubes cooled at -15°C . and packed with stainless steel wire-mesh saddles. All of the aforementioned equipment was glass or glass-lined, and it had been purified by baking before assembly followed by being flushed with dry nitrogen to exclude water after assembly.

B. Copolymerization

The formaldehyde gas, purified by the above procedure, was passed at about 3 parts per minute into the top of a baffled polymeri-

zation vessel which was fitted with a stirrer to provide violent agitation of the liquid contents. An exit tube from the vessel was connected in series, first, with an empty trap, and then with a trap partly filled with an inert liquid through which the off-gas could bubble. The final bubbler served to indicate the rate of gas absorption in the polymerization vessel.

Prior to connecting the polymerization vessel with the rest of the equipment, the vessel was charged with 467 parts of cyclohexane which had been freshly dried by passage through a silica gel column. Ten parts of vacuum-dried polytetramethylene glycol, $\text{HO}-(\text{CH}_2)_n-\text{OH}$, having a molecular weight of 7000, as calculated from hydroxyl number, was added to the vessel. Seventy-eight parts of solvent was distilled from the vessel to remove traces of water. The vessel was then cooled and connected with the rest of the equipment as described above.

The vessel was surrounded with a water bath at 25°C . to control the temperature of the reaction. The agitator was started and when the medium was saturated with formaldehyde, as shown by the final bubbler, 0.005 part of dimethyldi(70% octadecyl, 30% hexadecyl)ammonium acetate in cyclohexane solution was injected into the reaction medium as a polymerization initiator. Absorption of the gaseous formaldehyde was so rapid that the stirrer was run only part time during the following two minutes in order to prevent the liquid in the final bubbler from being sucked back into the empty trap. Fourteen minutes after the addition of the quaternary ammonium initiator, the polymerization vessel was disconnected, and the slurry of copolymer in cyclohexane was filtered.

The filter cake was washed with acetone and then continuously extracted several hours with acetone. The product was vacuum dried and found to weigh 34 parts. It analyzed 47.23% carbon which corresponds to a polytetramethylene glycol content of 27.1%.

C. Acetylation

An aliquot of the product was acetylated in solution by heating and stirring it with 18 parts (per part of copolymer) of acetic anhydride containing 0.04% of anhydrous sodium acetate in a nitrogen atmosphere in a closed system under reflux at a total nitrogen pressure of about 1.9 atmospheres until the polymer dissolved. At this point a thermometer located in a well extending into the solution registered 148°C . The excess nitrogen pressure was vented and the heating and stirring was continued under reflux at 1 atmosphere under a nitrogen blanket. Thirty minutes from the time at which the mixture first reached 138°C ., the polymer was precipitated rapidly from solution by applying a vacuum to the system. The polymer was filtered, exhaustively washed with acetone, water, and

acetone again and finally stabilized by incorporating into the copolymer 0.1% of di- β -naphthyl-p-phenylene-diamine, and 1% of a mixture of alcohol-soluble polyamides.

5 Copolymer recovery was 98%.

D. Properties

The acetylated copolymer had an inherent

viscosity of 1.3 as determined at 60° C. in 0.5% solution in parachlorophenol containing 2% of alpha-pinene. Other properties of the acetylated material and of other batches similarly prepared are summarized in the following table.

10

TABLE I

| Properties | Formaldehyde Copolymer | Polyoxymethylene Control |
|--|------------------------|--------------------------|
| Syringe stability (222° C., ml./g.) 10—20 min. | 2—4 | 2.5 |
| Flow No., g./10 min. at | | |
| 5 min. | 0.2—2.2 | 2.1 |
| 10 min. | 0.2—2.2 | 2.1 |
| Crystallinity, % | 40 | 65 |
| Film brittleness temp., °C. | —105 to —120 | —80 to —110 |
| Clarity | Good | Poor |
| Melting point, °C. Initial | 138; 162 | 173 |
| Main | 170 | — |
| Final | 178 | 178 |

15 The syringe stability is a measure of thermal stability. In this test, a 0.75 inch diameter disk is cold-pressed from 0.6—0.7 g. of dry polymer at room temperature and a total pressure of 12,000 lbs. for two minutes. The disk is
20 kept in a dry bottle until it is transferred to a 50 ml. syringe. The syringe is flushed with nitrogen and partly filled with an oxidation and heat-resistant silicone oil having a freezing point of —50° C. and a viscosity of 149 centistokes at 25° C. All but about 5 ml. of the oil is extruded, and the end of the syringe is closed with a polytetrafluoroethylene plug. The syringe is placed in a 222° C. vapor bath and the volume of gas evolved from the disk
25 is recorded at intervals by observing the movement of the syringe piston. The results are expressed in terms of milliliters of gas evolved per gram of polymer during specified time intervals. Values of less than 5 between
30 10 and 20 minutes indicate a high order of thermal stability. These results are achieved only when the polymers are acetylated and stabilized as described above.

35 The flow number is determined in an extrusion test in which about 6 g. of polymer is heated in a cylinder at 200° C. The cylinder is fitted at the bottom with an orifice having a diameter of 0.0413 inch and a length of 0.158 inch. The cylinder is equipped with a tight-
40 fitting piston having diameter of 0.373 inch.

The piston is weighted to a total mass of 5060 g. The orifice is closed for the first 4.5 minutes with a polytetrafluoroethylene plug. The plug is removed and the polymer which is extruded during one-minute intervals between
50 5 and 10 minutes is cut off and weighed. The weight of polymer extruded between 5 and 6 minutes is plotted at 5.5 minutes on a plot of weight versus time. The other extruded portions are similarly plotted and a curve is
55 drawn through the points. From the curve the flow rates at 5 and 10 minutes are read. These values are multiplied by ten to give so-called flow numbers expressed in g./10 minutes at 5 and 10 minutes, respectively. Polymers which
60 have flow numbers in the neighbourhood of 2 are well-suited to injection molding.

Crystallinity is determined with an x-ray diffractometer which records the reflections of the crystalline and amorphous portions of the polymer. The areas under the crystalline and amorphous peaks are determined and the percent crystallinity calculated therefrom. For these tests films were pressed at 190° C. and
65 allowed to cool slowly to 150° C. before removal from the press. Polyoxymethylene homopolymer under these conditions is seldom less than 65% crystalline. The value of 40%
70 for the block copolymer represents a substantial reduction of crystallinity as compared with
75 polyoxymethylene.

- 5 The film brittleness temperature test comprises cooling a film strip successively to lower and lower temperatures and creasing it under carefully controlled conditions between the jaws of an oversized spring-loaded clothespin. The creasing is accomplished by uniformly and slowly allowing the clothespin jaws to shut during the cooling period. The temperature at which about half of the strips in a series break is taken as the film brittleness temperature. 10 The film for this test is prepared by pressing 1.15 g. of vacuum dried polymer in a 2.5 inches x 0.5 inch bar mold at 40,000 lbs. total pressure for 1.5 minutes. The bar is placed in 15 a 1½ inches x 2½ inches x 10 mil-thick film frame and pressed between sheets of aluminum foil at 40,000 lbs. total pressure for 1.5 minutes in a press preheated to 195° C. The press is cooled with water and the film removed. Injection molded articles prepared from polymers which have a film brittleness temperature of less than -70° C. have high toughness and are, therefore, suitable for use in a variety of applications. 20
- 25 Melting points were determined with a microscope equipped with a hot stage and crossed Nicol prisms.
- 30 Additional properties of films and bars prepared from the acetylated and stabilized product are shown in the following two tables.

TABLE II

Properties of Films

| Properties | Formaldehyde Copolymer | Polyoxymethylene Control |
|---|------------------------|--------------------------|
| Tear strength, g./mil | 7.5 | 4.0 |
| Moisture permeability (g./sq. m./day/mil) | 12,000 | 500—2,000 |
| Impact strength, kg. cm./mil | 12.4 | 5 |
| Modulus, lbs./sq. in. | 68,000 | 400,000 |
| Tenacity, lbs./sq. in. | 3000 | 6000—10,000 |
| Elongation, % | 22 | 4—10 |

TABLE III

Properties of Molded Bars

| Properties | Formaldehyde Copolymer | Polyoxymethylene Control |
|--|------------------------|--------------------------|
| Method of molding | Compression | Injection |
| Izod impact, ft. lb./in. of notch | 4.8 | 2.8 |
| Rockwell hardness | R69 | R120 |
| Yield strength, lbs./sq. in. | 5100 | 10,000 |
| Tenacity, lbs./sq. in. | 4790 | 9500 |
| Elongation, % | 20—140 | 95 |
| % water absorption at 50% relative humidity and 23° C. | 0.23 | 0.13 |

EXAMPLE II

A polymerization vessel, as described in Example I, was charged with 8.5 parts of a vinyl acetate copolymer containing 5% crotonic acid. Traces of water were removed from the copolymer by evacuating the flask at 0.2 mm. at 100°—110° C. for 3 hours. Five hundred twenty-eight parts of reagent benzene was passed through a silica gel column and introduced directly into the polymerization flask. Eighty-eight parts of liquid was distilled from the flask to reduce the water content still further.

The flask was cooled to room temperature and connected with the monomeric formaldehyde generator described in Example I. The agitator was started and in 3 minutes, during which the reaction medium became saturated with formaldehyde, 0.0005 part of the quaternary ammonium initiator of Example I was injected. Agitation was continued and formaldehyde was passed into the flask continuously during the next 10 minutes, while the flask was cooled externally with a water bath at 25° C.

The resultant slurry was filtered and the filter cake was washed and extracted continuously with acetone for several hours. The product was vacuum dried and extracted three times with water at 60°—80° C. to remove remaining traces of unreacted vinyl acetate/crotonic acid copolymer. The product was then washed with acetone and vacuum dried. It had a weight of 24 parts. The product analyzed 45.06% carbon which corresponds to a content of vinyl acetate/crotonic acid copolymer of 32%.

An aliquot of the formaldehyde copolymer was acetylated as described in Example I and stabilized with 0.1% di- β -naphthyl-p-phenylenediamine. The acetylated material had an inherent viscosity of 1.75 (determined at 60° C. on a 0.5% solution in para-chlorophenol containing 2% α -pinene), flow numbers of 1.7 and 1.3 g./10 minutes at 5 and 10 minutes, respectively, and a syringe stability of 46 ml./g. between 0 and 10 minutes. In a film pressing test at 200° C. for 5 minutes wherein 0.50 g. of polymer was pressed at 3000 lbs. total pressure between sheets of aluminum foil, the acetylated material lost 4.4% of its weight. This compared with a loss of 0.22% for the copolymers of Example I and for values up to 1.4 for polyoxymethylene homopolymer controls.

When pressed at 190° C., the acetylated product formed a tough film. A film having a thickness of 3 mils could be manually creased at 180° without cracking.

EXAMPLE III

A polymerization vessel was charged with 3.4 parts of a polymeric material having primary amino end groups. The amino polymer had been prepared by cyanoethylation and reduction of a polytetramethylene glycol having a molecular weight of at least 500. It had

a neutral equivalent of 1700. Traces of water and volatile materials were removed from the vessel by evacuation at about 0.2 mm. pressure at 100—110° C. Four hundred sixty-seven parts of cyclohexane was passed through a silica gel column and introduced directly into the polymerization vessel. Seventy-eight parts of liquid was distilled out as in preceding examples. The flask was cooled to room temperature and connected with the formaldehyde generator described in Example I.

The agitator was started and formaldehyde was passed in during a period of 10 minutes during which polymerization occurred without the addition of a quaternary ammonium initiator as in the preceding examples. The polymer which had formed was filtered off, washed with acetone and continuously extracted several hours with acetone. The copolymer was vacuum dried and found to weigh 20 parts. It analyzed 42.58% carbon corresponding to a comonomer content of 9.7%.

An aliquot of the product was acetylated as in Example I and stabilized as in Example II. The acetylated material had an inherent viscosity of 1.41 in parachlorophenyl as described in previous examples. Its flow numbers at 5 and 10 minutes, respectively, were 1.5 and 7.3 g./10 minutes. Its syringe stability was 38 ml./g. between 0 and 10 minutes. It lost 4.1% in weight in the 200° C./5 minutes/3000 lbs. film test (Example II). A 2-mil film pressed at 190° C. was tough as determined by the creasing test described in Example II.

EXAMPLE IV

A polymerization vessel was charged with 4 parts of a methyl methacrylate/vinyloxyethylamine copolymer having a neutral equivalent of 4100. Five hundred twenty-seven parts of reagent benzene was passed through a silica gel column and introduced directly into the polymerization vessel. Eighty-eight parts of liquid was distilled from the vessel as described in the preceding example. The vessel was cooled to room temperature and connected with the formaldehyde generator described in Example I.

The agitator was started and formaldehyde passed in during a period of 11 minutes while the vessel was cooled with a water bath at 26° C. The polymer which had formed was filtered off and washed and extracted with acetone as described in Example I. The extracted polymer was vacuum dried and found to weigh 25.4 parts. It analyzed 41.70% carbon which corresponds to a comonomer content of 8.6%. It lost no weight in the 200°/5'/3000 lbs. film test and had a syringe stability of 12 ml./g. at 10—20 minutes. Its inherent viscosity in para-chlorophenol was 1.96, and it was formed into a tough film.

EXAMPLE V

A polymerization vessel was charged with 10 parts of vinyl acetate/allyl acetoacetate copolymer which, on the basis of its carbonyl

number, contained 90% vinyl acetate by weight. Five hundred twenty-seven parts of reagent benzene was passed through a silica gel column and introduced directly into the polymerization vessel. As in previous examples, 88 parts of liquid was distilled from the vessel, the vessel was cooled and connected with the formaldehyde generator.

The agitator was started and formaldehyde was passed in during three minutes to saturate the medium. The quaternary ammonium initiator of Example I, in the amount of 0.0005 part, was injected into the vessel and formaldehyde was passed in for an additional 10 minutes, while the reaction vessel was cooled with a 27° C. water bath. Gas absorption was so rapid during most of this time that the stirrer was run only part time. The insoluble polymer which had formed was filtered off, washed with acetone and extracted with acetone as described previously. The extracted polymer was vacuum dried and found to weigh 42.2 parts. It analyzed 44.3% carbon corresponding to a comonomer content of 26.9%. It had an inherent viscosity in para-chlorophenol of 1.66%.

An aliquot of the product was acetylated as described in Example I and stabilized as in Example II. The acetylated material had a syringe stability of 25 ml./g. between 10 and 20 minutes and flow numbers of about 0.1 g./10 minutes at both 5 and 10 minutes. It lost only 0.34% in weight in the 200° C./5 minutes/300 lbs. film test described in Example II. A 7.5-mil film pressed at 190° C. was tough as judged by the creasing test described in Example II. The acetylated material was incompletely soluble in either p-chlorophenol or dimethylformamide.

EXAMPLE VI

A polymerization vessel was charged with 10 parts of a polytetramethylene glycol having a molecular weight of about 7000, as determined from hydroxyl number. The vessel was evacuated at about 0.2 mm. for 4 hours at 100–110° C. The vessel was cooled and 467 parts of cyclohexane, freshly passed through a silica gel column, was introduced. Seventy-eight parts of liquid was distilled from the vessel, as described previously. The vessel was cooled and connected with the formaldehyde generator described in Example I; however, the generator was run at only about 75% of the rate given in Example I.

The agitator was started and after 5 minutes 0.002 part of the quaternary ammonium initiator of Example I was injected. Stirring and introduction of formaldehyde were continued for an additional 10 minutes. The polymerization mixture was filtered and the filter cake was continuously extracted with acetone for several hours. The extracted material was vacuum dried and found to weigh 14 parts. It analyzed 54.21% carbon, which corresponds to a polytetramethylene glycol content of

53%. After acetylation its inherent viscosity was 0.9.

Another copolymer, similarly prepared, analyzed 52.80% carbon, corresponding to a comonomer content of 48.0%. After acetylation it had an inherent viscosity in para-chlorophenol of 1.04, a film brittleness temperature of –118° C., syringe stabilities of 11 ml./g. between 10 and 20 minutes and 6.7 ml./g. between 80 and 90 minutes, and a flow number of 15 g./10 minutes at 5 minutes. It lost 0.60% in weight in the 200° C./5 minutes/3000 lbs. film pressing test.

EXAMPLE VII

A polymerization vessel was charged with 6.25 parts of a vinyloxyethylamine/isobutyl methacrylate copolymer, having a neutral equivalent of 3160, and 527 parts of reagent benzene, freshly passed through a silica gel column. Eighty-eight parts of liquid was distilled from the vessel to remove traces of water, as described previously. The vessel was cooled and connected with a formaldehyde generator as described in Example I.

The agitator was started and after 5 minutes 0.0005 part of the quaternary ammonium initiator of Example I was injected. Formaldehyde was passed in and agitation was continued for seven more minutes, during which time the reaction vessel was cooled with a 29° C. water bath. During this time gas absorption was so rapid that the stirrer was operated only part time. The reaction mixture became very thick. It was filtered and washed with acetone, and continuously extracted with acetone, as described previously. The polymer was vacuum dried and found to weigh 26 parts. It analyzed 41.04% carbon, which corresponds to a comonomer content of 3.8%.

An aliquot of the product was acetylated as described in Example I and stabilized as described in Example II. The acetylated material had an inherent viscosity in para-chlorophenol of 2.4, flow numbers of 0.1 and 0.1 g./10 minutes at 5 and 10 minutes, respectively, and a syringe stability of 10.1 ml./g. between 10 and 20 minutes. It lost only 0.16% in weight in the 200° C./5 minutes/3000 lbs. film test, as described in Example II. A film of 4-mil thickness, pressed at 190° C. was tough. The material had a film brittleness temperature (determined as described in Example I) of –70° C.

Repetition of Example I using a castor oil modified glyceryl triphthalate resin as the comonomer produced a copolymer, a portion of which was soluble in benzene while the other portion was insoluble in benzene. The benzene-insoluble portion had an inherent viscosity in para-chlorophenol of 2.4, a flow number of 0.4, and a syringe stability of 16.4 ml./g. between 10 and 20 minutes. The product analyzed 47.32% carbon, which corresponds to an alkyd resin content of 25.5%.

The benzene-soluble portion analyzed 66.5% carbon which corresponds to a formaldehyde content of about 8%.

Products varying widely in molecular weight were also obtained using as the comonomer, in the process of Example I, a stearic acid modified glyceryl triphthalate resin, polyethylene glycol phthalate, cellulose acetate having a degree of substitution of 2.9, N-isobutyl polyhexamethylene adipamide, a silicone (polydimethyl siloxane), and polydioxolane.

The preformed polymers which are operable in the preparation of the products of this invention are those polymers which are chemically different from polyoxymethylene, which are soluble in organic solvents, which have a molecular weight of at least 500, and preferably of at least 1000, and which contain active hydrogen atoms, as determined by the Zerewitinoff method [Ber. 40, 2026 (1927), J. Am. Chem. Soc. 49, 3181 (1927)]. Examples of such polymers include polyglycols other than polymethylene glycol, e.g., polyethylene and polybutylene glycols, polythiols, e.g., polybutylenethiols, reduced ethylene/carbon monoxide copolymers, reductively aminated ethylene/carbon monoxide copolymers, vinyl acetate/acrylic acid and vinyl acetate/methacrylic acid copolymers, reduced methyl methacrylate/acrylonitrile copolymers, methyl acrylate/vinylxypropylamine copolymers, reduced butadiene/acrylonitrile copolymers, acrylonitrile/methallylacetoacetate copolymers and reduced styrene/cyanoethylacrylate copolymers.

In general, the copolymers of this invention may vary in the weight ratio of formaldehyde preformed polymer from 99:1 to 10:90.

In practice, the comonomer is dissolved in the reaction medium and the formaldehyde is passed into the space above the agitated solution. As an alternative, the formaldehyde may be injected into the agitated comonomer solution.

The polymerization process, in general, is that described and claimed in our United Kingdom Patent Specification No. 753,299.

The amount of reaction medium can be from 1.5 to 1000 or more times the weight of the monomeric formaldehyde being polymerized, depending on, among other things, whether a batch or continuous process is being utilized. Because good results are obtained when the reaction medium is 4-100 times the weight of the formaldehyde being polymerized, that constitutes the amount of reaction medium usually used.

The polymerization is effected in the presence of one or more initiators for the polymerization of formaldehyde to polyoxymethylene. Examples of such initiators are the trihydrocarbonphosphines, arsines, and stibines disclosed in our United Kingdom Patent Specification No. 742,135; the tertiary amine-

containing polymers disclosed in our United Kingdom Patent Specification No. 744,336; the metal carbonyls disclosed in our United Kingdom Patent Specification No. 766,524; the metal organic compounds disclosed in our United Kingdom Patent Specification No. 766,629; and the onium salts, including quaternary salts and quaternary phosphonium salts, disclosed in our United Kingdom Patent Specification No. 793,673. The preferred initiators are the quaternary ammonium carboxylates.

As shown in the working examples, acylation leads to improved thermal stability and this after-treatment is therefore generally given the polymer if its ultimate use entails resistance to heat degradation.

The amount of formaldehyde polymerization initiator can vary from 0.00001 to 0.03% or more by weight of the reaction medium.

The polymerization of the formaldehyde is effected at temperatures which can be as low as the freezing point of the reaction medium or as high as the boiling point of the reaction medium. The particular temperature selected depends upon the initiator used, reaction medium, and other conditions. The temperature selected is that at which formaldehyde polymer is formed rapidly and with minimum of apparatus requirements. As a rule, these conditions are fulfilled in the range of -50° to $+50^{\circ}$ C. and this, therefore, embraces the preferred temperature range.

Monomeric formaldehyde from any source can be used in the practice of this invention. A convenient way for obtaining monomeric formaldehyde is by pyrolyzing alphapolyoxymethylene, or a hemiformal. In any case, before introducing the monomeric formaldehyde into the polymerization zone it should be rigorously purified, as described in Example I, or in any other manner which will reduce the concentration of water and all other impurities to less than 0.1%, while the remainder is formaldehyde.

The reaction medium is preferably one which is a non-solvent for the formaldehyde copolymer but is a solvent for the preformed polymer. The medium is also one which remains liquid under the temperature conditions used in the polymerization and which is essentially anhydrous. Alkanes of the C_3 to C_{10} range and mixtures thereof are preferred reaction media because of their availability and low cost, and because they fulfill the aforementioned requirements. In place of these, there can be used other saturated hydrocarbons such as cyclohexane, methyl cyclohexane and isobutane.

Reaction media which dissolve appreciable amounts of monomeric formaldehyde can also be used. Specific examples are dioxane, benzene, toluene and acetonitrile.

As previously stated, the structure of the

copolymers of this invention is not known, but it is believed that they are made up of segments, or blocks, formed by growing formaldehyde chains from the active hydrogen-containing polymer structure.

The block copolymers of the invention yield tough clear sheets and moldings, particularly structures, such as, fibers, films, and bristles and other articles made from synthetic resins. These formaldehyde copolymers possess a high order of thermal stability and retain toughness on aging. They are therefore valuable in commerce and are the first known copolymers containing polyoxymethylene chain units.

WHAT WE CLAIM IS:—

1. A block copolymer comprising 99%—10% by weight of one or more polyoxymethylene units, said units having a molecular weight of at least 4000, chemically joined to 1%—90% by weight of one or more polymeric units, which units are chemically different from polyoxymethylene, have a molecular weight of at least 500, are soluble in organic solvents and contain active hydrogen atoms as determined by the Zerewitinoff method.

2. A block copolymer according to Claim 1, which comprises one or more polyalkylene glycol units.

3. The block copolymers substantially as hereinbefore described.

4. A method of preparing block copolymers of polyoxymethylene, which comprises polymerizing substantially pure formaldehyde in the presence of one or more polymerization initiators and an organic solvent solution of a

polymeric unit which is chemically different from polyoxymethylene, has a molecular weight of at least 500 and contains active hydrogen atoms as determined by the Zerewitinoff method.

5. A method according to Claim 4, which comprises polymerizing formaldehyde in the presence of a solution of one or more alkylene glycol polymers.

6. A method according to Claim 4 or Claim 5, in which formaldehyde gas of a purity of at least 99.9% is continuously absorbed in the organic solvent solution in the presence of a formaldehyde polymerization initiator, such as a quaternary ammonium salt, until and as long as polymeric particles form and are precipitated in the solution, the temperature of the reaction being from -50°C . to $+50^{\circ}\text{C}$.

7. A method according to any of Claims 4—6, in which the polyalkylene glycol unit employed has a molecular weight of at least 1000, the organic solvent is a liquid alkane having from 5—10 carbon atoms per molecule and the formaldehyde polymerization initiator is a quaternary ammonium carboxylate.

8. A method according to any of Claims 4—7, in which the resulting block polymer is thereafter acylated as by treatment with a carboxylic acid anhydride such as acetic anhydride.

9. The method of preparing block copolymers substantially as set forth in the foregoing Examples.

PAGE, WHITE & FARRER,

Chartered Patent Agents,

27 Chancery Lane, London, W.C.2.

Agents for the Applicants.